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A novel CoP/MoS$_2$-CNTs hybrid catalyst with Pt-like activity for hydrogen evolution

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A novel and highly active hybrid catalyst for the hydrogen evolution reaction (HER) that is constructed by *in situ* growth of CoP on the surface of MoS$_2$ and CNTs. The CoP/MoS$_2$-CNTs hybrid catalyst exhibits Pt-like catalytic activity for the HER with overpotential close to zero, Tafel slope of 42 mV·dec^{-1} and good stability, which is the best among all the non-noble metal catalysts.

Nowadays, it is urgent to search alternative energy with the exhaustion of unrenewable resources such as fossil fuels and the increase of environmental pollution problems. Hydrogen, as a secondary energy, which can be considered as the most perfect green energy with efficient, clean, safe and others advantages in the current energy systems[1]. Right now, with the mature of electrolysis of water technology, it will become the main ways to produce hydrogen[2]. Pt-based noble metal catalysts are the most efficient hydrogen evolution reaction (HER) catalyst, but the high price and the shortage of resource limited their industrial application3. Therefore, the scientists have focused on the development of highly efficient non-noble metal electrocatalysts to replace Pt-based materials.

Up to now, both experimental and computational studies have demonstrated that MoS$_2$ can be considered as a promising catalyst with high HER activity[4]. The catalytic activity originate from the exposed (10-10) planes on the edge of MoS$_2$[5], therefore, more and more research focused on the enhancement of exposed edge active sites, which produce all kinds of novel MoS$_2$-based materials with high catalytic activity. For example, Pu et al.[6] designed a 3D macroporous MoS$_2$ thin film on Mo foil as a highly catalytic active HER catalyst. Xie et al.[7] designed a novel strategy to enhance catalytic active edge sites by controlling defect engineering in MoS$_2$ nanosheets. In spite of significant success, the design and synthesis of MoS$_2$-based catalysts with excellent catalytic activity and stability are still challenging for the HER.

In recently years, transition-metal phosphide (TMPs), especially Co-based phosphides, have been widely used in HER[8]. Yang et al.[9] reported that CoP nanosheet assembly grown on carbon cloth can be used as a highly active catalyst for hydrogen evolution. Liu et al.[10] synthesized a highly nanohybrid catalyst that composed of carbon nanotubes (CNTs) decorated with CoP by a low-temperature phosphidation method. Recently, the HER activity of CoP can be improved greatly after combining Ni$_2$P, and the synergetic coupling effect between CoP and Ni$_2$P was contribute to the improvement[11]. Similar promoted effects also have been demonstrated on CoS$_2$@MoS$_2$,[12] MoS$_2$/CoSe$_2$[13] and MoO$_3$/MoS$_2$[14] hybrid catalysts for hydrogen evolution. Therefore, this work point to the possibility to design novel and efficient HER catalysts by combining the promising CoP and MoS$_2$. We found the HER catalytic activity can be enhanced remarkably after combining (the data were shown in this work). In order to further improve the catalytic activity, the as-synthesized CoP/MoS$_2$ hybrid was decorated using CNTs due to the huge surface area and high electrical conductivity.

Herein, we report a novel HER hybrid catalyst with Pt-like activity that is constructed by *in situ* thermal decomposition growth of CoP nanorods (NRs) on the surface of MoS$_2$ and CNTs (denoted as CoP/MoS$_2$-CNTs). It is very nonintuitive that the as-synthesized CoP/MoS$_2$-CNTs hybrid catalyst shows an onset potential close to commercial 20% Pt/C catalyst and a small Tafel slope of 42 mV·dec^{-1} as well as good stability, exhibiting the best performance among all the non-noble metal HER electrocatalysts. This study provides a novel strategy for designing non-noble metal electrocatalysts with improved HER performance to replace the state-of-the-art noble metal catalysts.

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The crystalline phase of the CoP/MoS_2-CNTs hybrid catalyst was confirmed by X-ray diffraction (XRD) (Fig. 1a). Four diffraction peaks at 31.8°, 46.4°, 48.2° and 52.3° were observed, which can be attributed to the (002), (112), (211) and (103) planes of orthorhombic CoP (PDF# 00-029-0497). The peaks at 14.4°, 29.1°, 32.7°, 33.5°, 35.9°, 39.6°, 44.1°, 49.8°, 56°, 58.4°, 60.2°, 62.5°, 70.1° and 72.8°correspond to the (002), (004), (100), (101), (102), (103), (104), (105), (106), (110), (008), (107), (108) and (203) planes of hexagonal MoS_2 (PDF# 01-087-2416). In addition, two peaks at 26.6° and 41.1° were observed, which can be assigned to the (002) and (101) planes of hexagonal graphite (PDF# 00-001-0640). The XRD patterns of pure MoS_2, CoP and CoP/MoS_2 hybrid catalyst were shown in Fig. S1. All these results confirmed the formation of CoP, CoP/MoS_2 and CoP/MoS_2-CNTs hybrid catalysts.

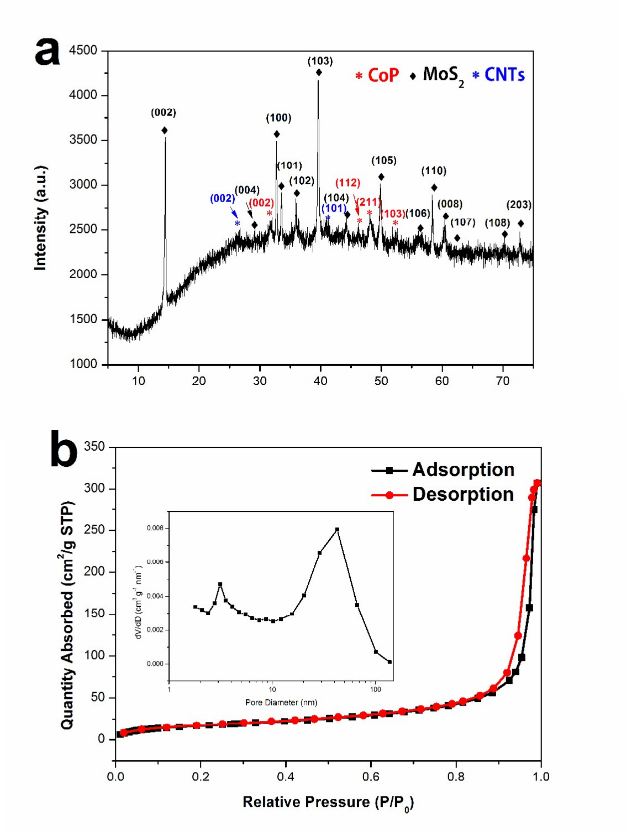

Fig. 1 (a) XRD and (b) N_2 sorption isotherm of the CoP/MoS_2-CNTs catalyst (Inset shows the pore-size distribution curve).

The textural property of the CoP/MoS_2-CNTs catalyst was characterized by N_2 sorption experiment (Fig. 1b). The CoP/MoS_2-CNTs catalyst exhibits a type-IV isotherm with a distinct H3-type hysteresis loop at the relative pressure from 0.8 to 1.0, revealing the macropores and mesopores natures[15]. The pore-size distribution curve also shows two narrow peaks at 3 and 43 nm, respectively, further confirming the existence of different pore type. The isotherm and pore-size distribution of pure MoS_2, CoP and CoP/MoS_2 hybrid catalyst were shown in Fig. S2. CoP/MoS_2 hybrid catalyst also shows a type-IV isotherm with a distinct H3-type hysteresis loop from 0.4 to 0.9. CoP also exhibits a type-IV isotherm but with H1-type hysteresis loop, suggesting the mesoporous characteristic. However, the adsorption branch and desorption branch of pure MoS_2 nearly not changed, no distinct hysteresis loop was observed, the isotherm belong to type-II, suggesting no macropores or mesopores existence. In addition, the CoP/MoS_2-CNTs hybrid catalyst exhibits the largest Brunauer-Emmet-Teller (BET) surface area (62.6 $m^2 \cdot g^{-1}$) among all the catalyst (Table S1), which indicates that it exposed the most active sites and exhibited the highest catalytic activity for HER.

The morphology of the catalysts was characterized by scanning electron microscope (SEM) and transmission electron microscopy (TEM). Pure MoS_2 only show conglomeration morphology (Fig. S3a-c). A large number of CoP in situ grown on the surface of MoS_2 can be observed from CoP/MoS_2 hybrid catalyst (Fig. S3d-f). Pure CoP exhibits nanorod-like structure with the length of about 18 nm (Fig. S4a). SAED image (Fig. S4b) shows clear diffraction rings, indicating a polycrystalline structure. SEM image of the CoP/MoS_2-CNTs catalyst (Fig. 2a) demonstrate that CoP was grown on lamellar MoS_2 and CNTs with well distribution and high density. TEM image (Fig. 2b) shows that the CoP exhibited typically nanorod shape structure with an average size of about 25 nm. It also can be seen that all the CoP NRs are grown on the MoS_2 and CNTs and no aggregated NRs are detected. The high-resolution TEM image (Fig. 2c) reveals a clear lattice fringe with the spacing of 2.93 Å, which can be attributed to the (011) crystalline face of CoP. The lattice fringes of MoS_2 also can be observed clearly. STEM and the energy dispersive X-Ray spectroscopy (EDX) elemental mapping images (Fig. 2d) reflecting a homogeneous distribution of Co, Mo, P, S and C elements on the CoP/MoS_2-CNTs catalyst. All these results strongly demonstrate the successful synthesis of the CoP/MoS_2-CNTs hybrid catalyst.

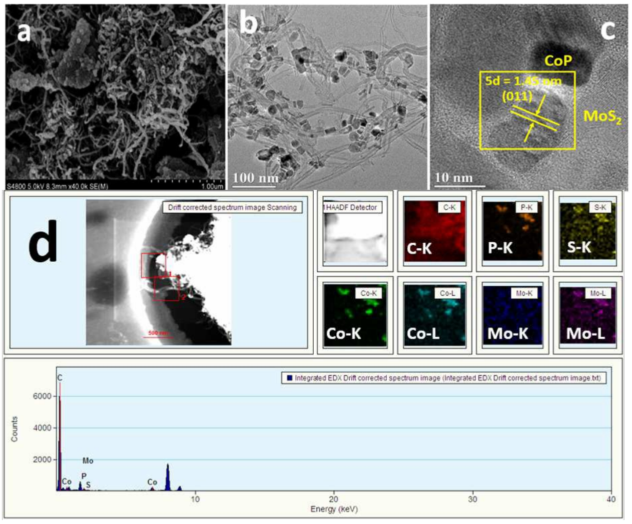

Fig. 2 (a) SEM, (b) TEM, (c) HRTEM and (d) STEM and the EDX elemental mapping images of the as-synthesized CoP/MoS_2-CNTs hybrid catalyst.

X-ray photoelectron spectroscopy (XPS) was used to study the chemical states of the CoP/MoS_2-CNTs catalyst (Fig. 3). For Mo 3d energy level, three peaks can be observed at 231.9, 228.8 and 225.9 eV, correspond to the Mo $3d_{3/2}$, Mo $3d_{5/2}$ and S 2s in MoS_2[16]. For S 2p energy level, two peaks were observed at 161.6 and 163 eV, correspond to the S $2p_{3/2}$ and S $2p_{1/2}$ in MoS_2. For Co $2p_{3/2}$ energy level, three peaks were observed at 777.7, 780.9 and 785.2 eV, which can be assigned to the Co-P, oxidized Co species and $2p_{3/2}$ satellite peak. Similarly, the others three peaks were observed at 792.7, 797.3 and 802.7 eV, which also can be attributed to the Co-P, oxidized Co species and $2p_{1/2}$ satellite peak[10]. For P 2p energy level, two peaks at 128.7 and 129.6 eV correspond to the P $2p_{3/2}$ and P $2p_{1/2}$ in CoP. Another peak at 132.5 eV can be assigned oxidized P species due to the catalyst was exposed in air. Furthermore, similar with the previous reported result, in CoP/MoS_2-CNTs hybrid catalyst, Co also have a small positive charge and P have a small negative charge, there is electron transfer between Co and P, which is beneficial for the HER process[17]. For comparison, the XPS results of pure MoS_2, CoP/MoS_2 and pure CoP catalysts were also provided (Fig. S5).

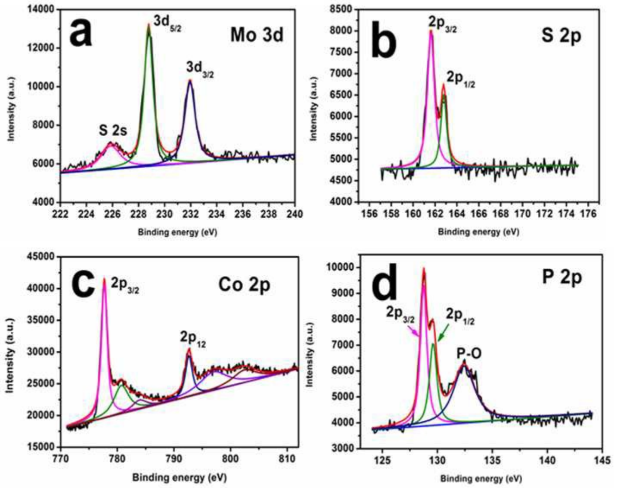

Fig. 3 XPS spectra of (a) Mo 3d, (b) S 2p, (c) Co 2p and (d) P 2p regions of the as-synthesized CoP/MoS_2-CNTs hybrid catalyst.

The as-synthesized CoP/MoS_2-CNTs hybrid catalyst are further evaluated as electrocatalysts at room temperature for HER in 0.5 M H_2SO_4 solution. The commercial pure MoS_2, CoP, CoP/MoS_2 and commercial 20 % Pt/C catalysts were also tested. Linear sweep voltammetry (LSV) curves (Fig. 4a) indicates that commercial pure MoS_2 shows poor HER performance with onset overpotential of 334 mV. Pure CoP NRs shows onset overpotential of 139 mV, indicating the higher catalytic activity than MoS_2. The catalytic activity can be improved remarkably after CoP grown on the MoS_2, the CoP/MoS_2 catalyst shows an overpotential of 96 mV. To our surprise, after the introduction of CNTs, the CoP/MoS_2-CNTs hybrid catalyst exhibits Pt-like catalytic activity for HER with overpotential close to zero and shows a large cathodic current density at small overpotential, which is the best among all the non-noble metal catalysts for HER. It can be clearly seen that the LSV curve of CoP/MoS_2-CNTs catalyst nearly coincide with commercial 20 % Pt/C catalyst. It only need 12 and 25 mV to reach the current densities of 10 and 20 $mA\cdot cm^{-2}$. All these results strongly demonstrate that the CoP/MoS_2-CNTs hybrid can be used as a high-efficient hydrogen evolution catalyst.

Fig. 4b shows the Tafel plot of the as-synthesized hybrid catalysts. The linear portions are fitted into the Tafel equation (η = b log j + a, where b is the Tafel slope), and the obtained Tafel slope were 159, 96, 87, 42 and 31 $mV\cdot dec^{-1}$ for the commercial pure MoS_2, CoP, CoP/MoS_2, CoP/MoS_2-CNTs and commercial 20 % Pt/C catalysts, revealing a Volmer-Heyrovsky mechanism of the CoP/MoS_2-CNTs hybrid catalyst. The exchange current density (j_0), which reflects the inherent HER catalytic activity, was calculated from the Tafel plot using an extrapolation method (Fig. S6 and Table S2). The CoP/MoS_2-CNTs catalyst shows the largest j_0 of 3.16 $\mu A\cdot cm^{-2}$ among all the as-synthesized catalyst, further indicating the highest electrocatalytic activity for HER.

To understand the origin of the superior activity of CoP/MoS_2-CNTs hybrid catalyst, we further test the double layer capacitance (C_{dl}) to estimate the effective electrochemical active surface area (ECSA) (Fig. S7), because C_{dl} is considered to be linearly proportional to ECSA, and the current density can be influenced by ECSA. The CoP/MoS_2-CNTs catalyst has much larger C_{dl} (12.24 $mF\cdot cm^{-2}$), which is about 28.5, 29.8 and 159 times than that of CoP/MoS_2, CoP, and pure MoS_2 catalysts (Fig. 4c), suggesting the remarkable catalytic active sites of the CoP/MoS_2-CNTs hybrid catalyst for HER. Moreover, the electrochemical impedance spectroscopy (EIS) test (Fig. 4d) indicates that the CoP/MoS_2-CNTs catalyst shows the lowest semicircle at the same overpotential of 200 mV, indicating the best electron transfer ability, further suggesting the highest HER activity.

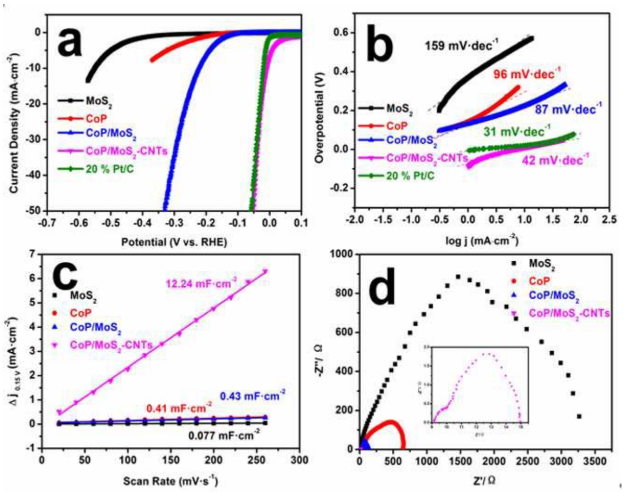

Fig. 4 (a) LSV curves (iR corrected), (b) Tafel plots, (c) The relationship between the current density variation and scan rate and (d) Nyquist plots of the pure MoS_2, CoP, CoP/MoS_2, CoP/MoS_2-CNTs catalysts (Inset in d shows the expansion of the high frequency region of CoP/MoS_2-CNTs catalyst).

Furthermore, the stability test of the as-synthesized CoP/MoS_2-CNTs hybrid catalyst was carried out at a scan rate of 100 $mV\cdot s^{-1}$ for 1000 cycles in 0.5M H_2SO_4, as shown in Fig. 5. It can be seen that, after 1000 cycles, the LSV curve show negligible loss in current density by comparing with the initial curve, indicating the excellent stability of CoP/MoS_2-CNTs hybrid catalyst in acid solution. Additionally, the time-dependent current density curve (inset Fig. 5) shows that the CoP/MoS_2-CNTs hybrid catalyst maintain the electrocatalytic activity for at least 60 000 s.

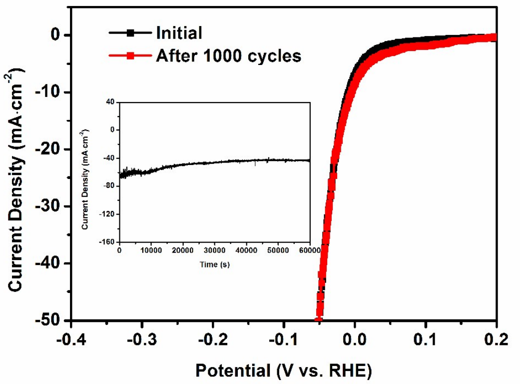

Fig. 5 LSV curves of the CoP/MoS_2-CNTs hybrid catalyst before and after 1000 cycles (Inset shows the time-dependent current density curve with a static overpotential of 50 mV).

The excellent Pt-like catalytic activity of the as-synthesized CoP/MoS_2-CNTs hybrid catalyst can be attributed to the following major reasons: (i) the synergistic effect between CoP and MoS_2 have great contribution to the high catalytic activity. MoS_2, not only as an active phase, but also as a support, which is beneficial for the grown of CoP NRs. TEM results indicates that CoP NRs were grown on the MoS_2 with high density and dispersion, which exposed more catalytic active sites and improved the HER performance. (2) After the introduction of CNTs, the BET surface area and electrical conductivity of CoP/MoS_2-CNTs hybrid catalyst can be increased gradually, both are beneficial for the hydrogen evolution. (3) XPS results indicates that Co and P in CoP has a partial positive and negative charge, respectively, which indicate that there is charge transfer from Co to P, suggesting the covalent character of Co-P bond. It has been reported that the hydrogen generation mechanism of CoP is similar with the hydrogenases[18]. Additionally, Sun group also reported that CoP exhibits high HER catalytic activity and feature a metal center (δ^+) with a pendant base P (δ^-) close to it[19]. The Co and P centers act as the hydride-acceptor and proton-acceptor, respectively, which promotes the HER process[20a]. In addition, the P centers also promote the formation of Co-H species, which is beneficial for hydrogen evolution by electrochemical desorption process[20b].

In summary, we report a novel hybrid catalyst with Pt-like activity for the HER that is constructed by *in situ* thermal decomposition growth of CoP NRs on the surface of MoS_2 and CNTs. The as-synthesized CoP/MoS_2-CNTs hybrid catalyst exhibits Pt-like catalytic activity for HER with overpotential close to zero and Tafel slope of 42 mV·dec^{-1}, which is the best among all the non-noble metal catalysts. It only need 12 and 25 mV to reach the current densities of 10 and 20 mA·cm^{-2}. This high-efficient catalytic activity nearly coincide with commercial Pt/C catalyst. The excellent catalytic activity is attributed to the strong synergistic effect between CoP and MoS_2 as well as the introduction of CNTs, which increased catalytic active sites and charge transfer ability. This study provides a novel strategy for designing novel and high-performance catalyst, which has a great potential application in water splitting.

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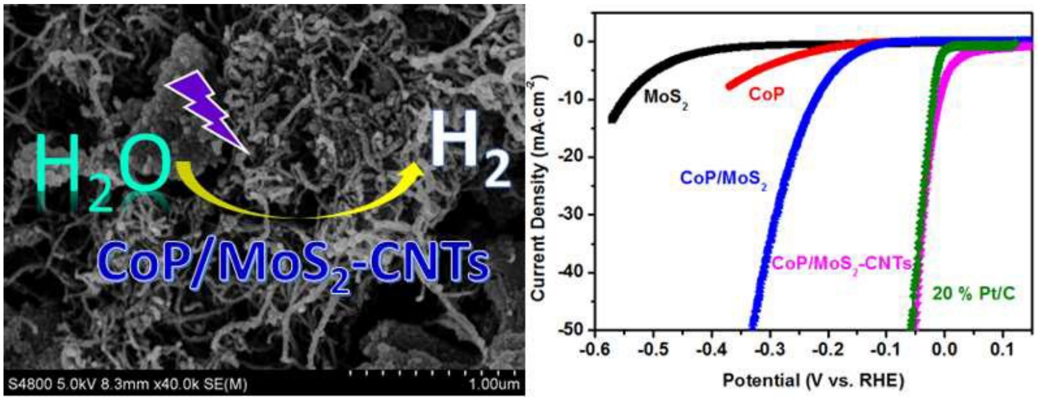
References

1 Y. Jiao, Y. Zheng, M. T. Jaroniec and S. Z. Qiao, *Chem. Soc. Rev.*, 2015, **44**, 2060-2086.
2 Y. Zheng, Y. Jiao, M. Jaroniec and S. Z. Qiao, *Angew. Chem. Int. Ed.*, 2015, **54**, 52-65.
3 E. Antolini, Energy Environ. Sci., 2009, **2**, 915-931.
4 (a) B. Hinnemann, P. G. Moses, J. Bonde, K. P. Joergensen, J. H. Nielsen, S. Horch, I. Chorkendorff and J. K. Nørskov, *J. Am. Chem. Soc.*, 2005, **127**, 5308-5309. (b) J. Huang, D. Hou, Y. Zhou, W. Zhou, G. Li, Z. Tang, L. Lia and S. Chen, *J. Mater. Chem. A*, 2015, **3**, 22886-22891. (c) W. Zhou, D. Hou, Y. Sang, S. Yao, J. Zhou, G. Li, L. Li, H. Liu and S. Chen, *J. Mater. Chem. A*, 2014, **2**, 11358-11364.
5 H. I. Karunadasa, E. Montalvo, Y. Sun, M. Majda, J. R. Long and C. J. Chang, *Science*, 2012, **335**, 698-702.
6 Z. Pu, Q. Liu, A. M. Asiri, Y. Luo, X. Sun and Y. He, *Electrochim. Acta*, 2015, **168**, 133-138.
7 J. Xie, H. Zhang, S. Li, R. Wang, X. Sun, M. Zhou, J. Zhou, X. W. Lou and Y. Xie, *Adv. Mater.*, 2013, **25**, 5807-5813.
8 (a) L. Ma, X. Shen, H. Zhou, G. Zhu, Z. Jia and K. Chen, *J. Mater. Chem. A*, 2015, **3**, 5337-5343. (b) M. Li, X. Liu, Y. Xiong, X. Bo, Y. Zhang, C. Han and L. Guo, *J. Mater. Chem. A*, 2015, **3**, 4255-4265.
9 X. Yang, A. Y. Lu, Y. Zhu, M. N. Hedhili, S. Min, K. W. Huang, Y. Han and L. J. Li, *Nano Energy*, 2015, **15**, 634-641.
10 Q. Liu, J. Tian, W. Cui, P. Jiang, N. Cheng, A. M. Asiri and X. Sun, *Angew. Chem.*, 2014, **126**, 6828-6832.
11 Y. Feng, X. Yu and U. Paik, *Chem. Commun.*, 2016, **52**, 1633-1636.
12 H. Zhang, Y. Li, T. Xu, J. Wang, Z. Huo, P. Wan and X. Sun, *J. Mater. Chem. A*, 2015, **3**, 15020-15023.
13 M. R. Gao, J. X. Liang, Y. R. Zheng, Y. F. Xu, J. Jiang, Q. Gao, J. Li and S. H. Yu, *Nat. Commun.*, 2015, **6**, 5982-5988.
14 Z. Chen, D. Cummins, B. N. Reinecke, E. Clark, M. K. Sunkara and T. F. Jaramillo, *Nano Lett.*, 2011, **11**, 4168-4175.
15 B. You, N. Jiang, M. Sheng and Y. Sun, *Chem. Commun.*, 2015, **51**, 4252-4255.
16 F. Li, L. Zhang, J. Li, X. Lin, X. Li, Y. Fang, J. Huang, W. Li, M. Tian, J. Jin and R. Li, *J. Power Sources*, 2015, **292**, 15-22.
17 E. J. Popczun, J. R. McKone, C. G. Read, A. J. Biacchi, A. M. Wiltrout, N. S. Lewis and R. E. Schaak, *J. Am. Chem. Soc.*, 2013, **135**, 9267-9270.
18 Y. Nicolet, A. L. de Lacey, X. Vrnede, V. M. Fernandez, E. C.Hatchikian and J. C. Fontecilla-Camps, *J. Am. Chem. Soc.*, 2001, **123**, 1596-1601.
19 (a) J. Tian, Q. Liu, A. M. Asiri and X. Sun, *J. Am. Chem. Soc.*, 2014, **136**, 7587-7590. (b) Z. Pu, Q. Liu, P. Jiang, A. M. Asiri, A. Y. Obaid and X. Sun, *Chem. Mater.*, 2014, **26**, 4326-4329.
20 (a) P. Liu and J. A.Rodriguez, *J. Am. Chem. Soc.*, 2005, **127**, 14871-14878. (b) W. Zhang, J. Hong, J. Zheng, Z. Huang, J. Zhou and R. Xu, *J. Am. Chem. Soc.*, 2011, **133**, 20680-20683.

Graphic Abstract



A novel hybrid catalyst with Pt-like activity for the hydrogen evolution reaction that is constructed by *in situ* growth of CoP on the surface of MoS_2 and CNTs.